Analytical estimate of effective charges at saturation in Poisson-Boltzmann cell models

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We propose a simple approximation scheme to compute the effective charge of highly charged colloids (spherical or cylindrical with infinite length). Within non-linear Poisson-Boltzmann theory, we start from an expression of the effective charge in the infinite dilution limit which is asymptotically valid for large salt concentrations; this result is then extended to finite colloidal concentration, approximating the salt partitioning effect which relates the salt content in the suspension to that of a dializing reservoir. This leads to an analytical expression of the effective charge as a function of colloid volume fraction and salt concentration. These results compare favorably with the effective charges *at saturation* (i.e. in the limit of large bare charge) computed numerically following the standard prescription proposed by Alexander *et al.* within the cell model.

I. INTRODUCTION

In colloidal suspensions, the charge ratio between the poly-ions (colloids) and the counter-ions or salt ions may be larger than 10^4. This considerable asymmetry invalidates most of standard liquid state theories. The concept of charge renormalization however allows to significantly simplify the description of such systems: the electrostatic coupling between the poly-ions and oppositely charged micro-species induces a strong accumulation (or "condensation") near the poly-ion surface. The idea is then to consider a colloid plus its "captive" micro-ions as an entity carrying an effective (or renormalized) charge $Z_{\rm eff}$, *a priori* much smaller than the bare charge $Z_{\rm bare}$. Consequently, except in the immediate vicinity of the colloids where linearization schemes fail, the interactions in the suspension are well described by Debye-Hückel-like linearized theories, provided that the bare charge is replaced by the renormalized one $Z_{\rm eff}$. Schematically, the linear effects of screening by an electrolyte induce a dressing of the bare Coulomb potential [$Z_{\rm bare}/r \to Z_{\rm bare} \exp(-\kappa r)/r$ where κ^{-1} is the Debye length, see below], while the non-linear effects of screening imply the identification $Z_{\rm bare} \exp(-\kappa r)/r \to Z_{\rm eff} \exp(-\kappa' r)/r$ (with possibly $\kappa' \neq \kappa$ [1]).

Several reviews discussing the notion of charge renormalization have appeared recently [1–4]. In the colloid science field this concept has been introduced by Alexander *et al.* [5] in the context of the Poisson-Boltzmann (PB) cell model, but had been widely accepted since the fifties in the field of linear polyelectrolytes [6,7]. The definition of an effective charge from the far field potential created by an isolated macro-ion in an electrolyte is unambiguous [2,8,9], at least for the simple cases of spherical or infinitely long cylindrical macro-ions we shall consider here, even if the case of less symmetric poly-ions deserves more attention (see e.g. [10]). Within a cell model, introduced to replace the complicated many body problem of colloids in solution by a simpler one-particle system [11–14], the definition of an effective charge is more elusive, but the celebrated proposal made by Alexander *et al.* amounts to find the optimal linearized PB potential matching the non-linear one at the cell boundary. The cell approach, which validity has been assessed by several studies [16–21], appears to provide a reasonable description of solutions containing mono-valent counter-ions [22–24]. The effective charge is obtained by integrating the charge density deduced from the linearized potential over the region accessible to micro-ions, or equivalently from Gauss theorem at the colloid's surface. Note that a renormalization of Z also implies a renormalization of the screening constant κ. For low poly-ion bare charges $Z_{\rm bare}$, linearizing PB equation is a valid approximation so that $Z_{\rm eff} \simeq Z_{\rm bare}$, whereas in the opposite limit of high bare charges, $Z_{\rm eff}$ was found numerically to saturate to a value independent of $Z_{\rm bare}$: $Z_{\rm eff} \simeq Z_{\rm sat}$. The saturation value $Z_{\rm sat}$ depends on the geometry of the colloid, the temperature or the quantity of added-salt. Unfortunately, no analytical prediction is available for these dependences.

In this letter, we propose an approximate analytical expression for the effective charge of spherical or rod-like macro-ions, as a function of macro-ion density or salt content. Our approach starts with an estimate of the saturation value of the effective charge in the infinite dilution limit, as deduced from recent analytical results [25]. In the case of finite colloidal dilution, the osmotic equilibrium of the suspension with a salt reservoir is modeled using a Donnan equilibrium approximation. This allows to derive a simple polynomial equation of degree 4 fulfilled by the *saturation value* $Z_{\rm sat}$ of the effective charge $Z_{\rm eff}$, in the case of a symmetric 1:1 electrolyte. In the limiting case of no added salt,

the above equation is easily solved analytically and provides results in quantitative agreement with the saturation effective charges following Alexander's prescription.

II. GENERAL FRAMEWORK AND METHOD

We consider first the situation of an isolated macro-ion of given surface charge density in a electrolyte of bulk density n_0 (no confinement). The solvent is considered as a medium of uniform dielectric (CGS) permittivity ε. Within Poisson-Boltzmann theory, the electrostatic potential, when assumed to vanish far from macro-ion obeys the equation

$$\nabla^2 \phi = \kappa_0^2 \sinh \phi, \tag{1}$$

where the screening factor κ_0 is defined as $\kappa_0^2 = 8\pi \ell_B n_0$ and the Bjerrum length quantifies the strength of electrostatic coupling: $\ell_B = e^2/(\varepsilon kT)$ ($e > 0$ denotes the elementary charge and kT is the thermal energy). A complete asymptotic solution of Eq. (1) has been obtained recently by Shkel $et\ al.$ [25] in spherical and cylindrical geometry. From the far-field behaviour of the corresponding solutions, one obtains after some algebra the effective charges at saturation

$$Z_{\text{sat}} \frac{\ell_B}{a} = 4\kappa_0 a + 6 + \mathcal{O}\left(\frac{1}{\kappa_0 a}\right) \quad \text{for spheres} \tag{2}$$

$$\lambda_{\text{sat}} \ell_B = 2\kappa_0 a + \frac{3}{2} + \mathcal{O}\left(\frac{1}{\kappa_0 a}\right) \quad \text{for cylinders.} \tag{3}$$

In these equations, a denotes the radius of the macro-ion under consideration, Ze the total charge in the case of spheres and λe the line charge density in the case of cylinders (with infinite length). Expressions (2) and (3) are the exact expansions of the saturation charges in the limit of large $\kappa_0 a$ but are in practice accurate as soon as $\kappa_0 a > 1$ (not shown).

Our goal is to translate these relations into expressions that would approximate the effective charges in confined geometry, where the macro-ion is enclosed in a cell [5]. To this aim, we first find an approximation for the relevant screening factor $\kappa_\star$ before inserting it into (2) and (3) making the substitution $\kappa_\star \leftrightarrow \kappa_0$. The implicit assumption is that the mean salt density in the cell is related to the effective charge in a similar manner as in the infinite dilution limit.

In confined geometry, PB equation still takes the form (1), where $\kappa_0 = (8\pi \ell_B n_0)^{1/2}$ should now be considered as the inverse screening length in a (neutral) salt reservoir in osmotic equilibrium with the solution, through a membrane permeable to micro-species (n_0 is thus now the salt density in the reservoir). It may be shown that the relevant screening factor in the cell is related to the micro-ions density at the cell boundary [8]:

$$\kappa_\star^2 = 4\pi \ell_B \left[\rho^+(R_{WS}) + \rho^-(R_{WS})\right]. \tag{4}$$

In this equation R_{WS} is the radius of the Wigner-Seitz (WS) confining cell. We have recently proposed an efficient prescription to compute $\kappa_\star$ without solving the complicated non-linear problem [8]. It is however impossible to deduce an analytical expression of $\kappa_\star$ from this approach and we resort to the following approximation. We assume that the micro-ion densities are slowly varying in the WS cell so that the mean densities $n^\pm$ provide a reasonable estimation of the boundary densities $\rho^\pm(R_{WS})$. We thus write

$$\kappa_\star^2 = 4\pi \ell_B(n^+ + n^-) = 4\pi \ell_B(2n^+ + Z_{\text{sat}}\rho), \tag{5}$$

where the last equality follows from the electroneutrality constraint (ρ is the density of colloids, assumed positively charged without loss of generality). Note that at the level of a linear theory, the effective charge Z_{sat} and not the bare one Z_{bare} enters this expression.

We now need to relate the mean densities $n^\pm$ to n_0, the concentration in the reservoir (the so called Donnan effect, see e.g. [26,14]). Chemical equilibrium imposes $\rho^+\rho^- = n_0^2$ at any point in the cell. We again assume this relation to hold for the mean densities, so that $n^+ n^- = n_0^2$. This leads to

$$\kappa_\star^4 = \kappa_0^4 + (4\pi \ell_B Z_{\text{sat}}\rho)^2. \tag{6}$$

Up to now the reasoning is quite general and independent of the geometry. For spheres with radius a and packing fraction $\eta = 4\pi\rho a^3/3 = (a/R_{WS})^3$, and for rods with packing fraction $\eta = (a/R_{WS})^2$, we obtain

$$(\kappa_\star a)^4 = (\kappa_0 a)^4 + (3\eta Z_{\text{sat}} \ell_B/a)^2 \text{ (spheres)} \quad \text{and} \quad (\kappa_\star a)^4 = (\kappa_0 a)^4 + (4\eta \lambda_{\text{sat}} \ell_B)^2 \text{ (cylinders)} \tag{7}$$

2

Supplementing these equations with the κ dependence of Z_{sat} obtained in Eq. (2) for spheres and (3) for cylinders, leads to an equation of degree 4 satisfied by $\kappa_\star$ (or equivalently Z_{sat}).

This equation can be solved analytically. We give the general solution in appendix A. However, without added salt (formally $\kappa_0 = 0$), the solutions of these equations take a particularly simple form:

$$Z_{\text{sat}} \frac{\ell_B}{a} = 6 + 24\eta + 12\sqrt{2\eta + 4\eta^2} \qquad (8)$$

$$\lambda_{\text{sat}} \ell_B = \frac{3}{2} + 8\eta + 2\sqrt{6\eta + 16\eta^2} \qquad (9)$$

We compare on Figs. (1) and (2), the results obtained following this route with the full PB estimate following Alexander's prescription. The latter involves a numerical resolution of the PB equation. Both the no-salt and the finite ionic strength case are considered. The agreement is seen to be quite good in view of the minimum number of ingredients involved in the present approach.

III. CONCLUSION

In this contribution, we propose a simple approximation scheme to compute the saturation value of the effective charge in concentrated suspensions of highly charged colloidal particles. Our estimate starts with an asymptotic expression of the effective charge in the infinite dilution limit, obtained from recent analytical results [25]. The case of finite colloidal dilution is described using a Donnan equilibrium approximation for the osmotic equilibrium of the suspension with a salt reservoir. This calculation leads to an analytical estimate of Z_{sat}, the saturation value of the effective charge, as a function of the density of colloids and salt concentration. Our starting points [Eqs. (2) and (3)] neglect contributions of order $(\kappa_0 a)^{-1}$ and become inaccurate for $\kappa a < 1$. This implies that our effective charges at finite density becomes less reliable in the salt free case for small packing fractions η. However, this is seen to occur for very small η only (see e.g. Fig. 1).

These results are obtained at the level of the mean-field Poisson-Boltzmann theory. We note however that the existence of a saturation value of the effective charge, Z_{sat}, independent of the bare charge, is indeed confirmed in more refined approaches in the *colloidal limit* $a \gg \ell_B$, with a the colloid size and ℓ_B the Bjerrum length (see e.g. Groot [22] using the primitive model). These results show moreover that PB theory becomes successful in the afore-mentioned colloidal limit, $a \gg \ell_B$ [22,20]. Eventually the saturation picture within PB theory is in quantitative agreement with experimental data for the osmotic pressure [27,28,8].

It is eventually instructive to reconsider the results reported by Alexander *et al.* in their original paper [5]. At a packing fraction $\eta = 0.125$, they find numerically a saturation value for Z_{eff} of the order of 15, in a/ℓ_B units (spherical colloid). On the other hand our expression (8) for the same η gives $Z_{\text{sat}} \ell_B / a = 9 + 3\sqrt{5} \simeq 15.7$, i.e. very close to the value found in [5]. Note that this number of 15 has subsequently been often quoted in the literature as a "standard" value of the effective charge. The saturation value of the effective charge however crucially depends on the colloid volume fraction, and the full density dependence of Z_{sat} should be taken into account in finite concentration cases.

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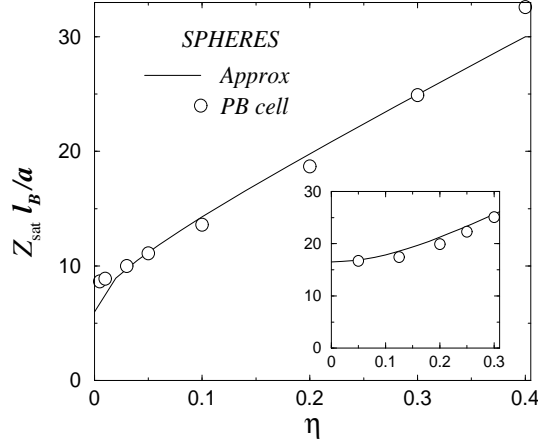[28] E. Raspaud, L. da Conceicao, and F. Livolant, Phys. Rev. Lett. **84**, 2533 (2000).

FIG. 1. Effective charge at saturation Z_{sat} (in units of radius over Bjerrum length ℓ_B), as a function of packing fraction for a spherical macro-ion of radius a enclosed in a concentric spherical cell of radius $a\eta^{-1/3}$. The situation is without added salt. The analytical expression (8) is shown by the continuous curve while the non-linear Poisson-Boltzmann values computed numerically following Alexander *et al.* [5] are represented with circles. Inset: same with added salt for $\kappa_0 a = 2.6$.
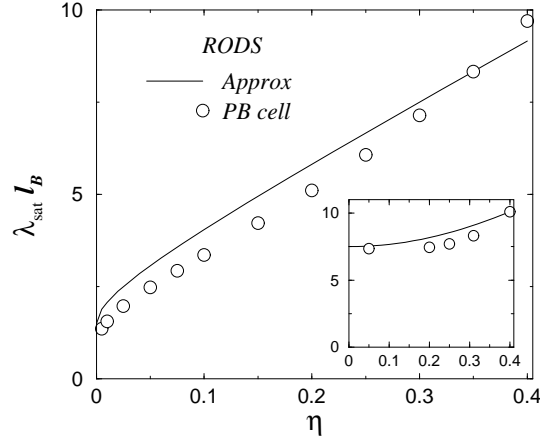
FIG. 2. Effective line charge density at saturation λ_{sat} (in units of $1/\ell_B$), as a function of packing fraction for a cylindrical macro-ion of radius a enclosed in a concentric cylindrical cell of radius $a\eta^{-1/2}$ (no added salt). The analytical expression (9) is shown by the continuous curve while the non-linear Poisson-Boltzmann values computed numerically following Alexander *et al.* [5] are represented with circles. The inset shows the same quantity with added electrolyte ($\kappa_0 a = 3.0$).

APPENDIX A: ANALYTICAL EXPRESSION FOR THE EFFECTIVE CHARGE

We give here the explicit expression for the effective charge as a function of the colloid packing fraction η and salt concentration in the reservoir, $n_0 = \kappa_0^2/8\pi\ell_B$.

Inserting Eqs. (2) or (3) into Eq. (7), one gets the quartic equation for $X = \kappa_\star a$:

$$X^4 = X_0^4 + \eta^2(\alpha + \beta X)^2 \tag{A1}$$

with $X_0 = \kappa_0 a$. Values for α, β are respectively $\alpha = 12$ and $\beta = 18$ for spheres, and $\alpha = 8$ and $\beta = 6$ for cylinders.

Let us introduce the following quantities :

$$
\begin{aligned}
\Lambda &= -12X_0^4 - 12\beta^2\eta^2 + \alpha^4\eta^4 \\
\Gamma &= 108\alpha^2\beta^2\eta^4 - 2\alpha^6\eta^6 - 72\alpha^2\eta^2(X_0^4 + \beta^2\eta^2) \\
\Phi &= -72X_0^4\alpha^2\eta^2 + 36\alpha^2\beta^2\eta^4 - 2\alpha^6\eta^6 \\
\Psi &= \frac{1}{3\,2^{1/3}}\left(\Phi + \sqrt{\Gamma^2 - 4\Lambda^3}\right)^{1/3} \\
\Theta &= \frac{\Lambda}{9\Psi} + \Psi
\end{aligned} \tag{A2}
$$

The solution $X = \kappa_\star a$ is then found as

$$\kappa_\star a = \frac{1}{2}\sqrt{\frac{2\alpha^2\eta^2}{3} + \Theta} + \frac{1}{2}\left(\frac{4\alpha^2\eta^2}{3} - \Theta + \frac{4\alpha\beta\eta^2}{\sqrt{\frac{2\alpha^2\eta^2}{3} + \Theta}}\right)^{1/2} \tag{A3}$$

The effective charge is then obtained by replacing this value for $\kappa_\star$ in Eq. (2) for spherical macro ions, and in Eq. (3) for rod-like macro ions.

In the no-added salt case, these expressions reduce to Eqs. (8) and (9), as indicated in the text.